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(54) HARD FILM, HARD FILM COATED TOOL AND HARD FILM COATED MEMBER EXCELLENT IN WEAR RESISTANCE

(57)Abstract:

PURPOSE: To produce a hard film excellent in oxidation resistance by (Al, Ti)(C, N), furthermore having high hardness and showing excellent wear resistance without deteriorating the base material adhesion characteristic of the TiN film. CONSTITUTION: The film formed on the surface of a base material has a chemical compsn. shown by $(Al_xTi_{1-x}Si_y)(N_2C_{1-z})$; where $0.05 \leq x \leq 0.75$, $0.01 \leq y \leq 0.1$ and $0.64 \leq z \leq 1$. The thickness of this hard film is preferably regulated to 0.1 to 20 μm , and in the case the same hard film is formed on the surface of the base material by an arc discharge-system ion plating method, the hard film coated tool and hard film coated member excellent in wear resistance can be obt'd.

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CLAIMS

[Claim(s)]

[Claim 1] It is the coat formed in a base-material front face ($N_z (Al_x Ti_{1-x-y} Si_y) C_{1-z}$).

However, the hard anodic oxidation coatings excellent in the abrasion resistance characterized by consisting of a chemical composition shown by $0.05 \leq x \leq 0.75$, $0.01 \leq y \leq 0.10$, $0.6 \leq z \leq 1$.

[Claim 2] The hard anodic oxidation coatings according to claim 1 whose thickness of a coat is 0.1-20 micrometers.

[Claim 3] A hard-anodic-oxidation-coatings covering tool and a hard-anodic-oxidation-coatings covering member excellent in the abrasion resistance characterized by coming to form a hard anodic oxidation coatings according to claim 1 or 2 in a base-material front face by the arc discharge method ion-plating method.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] this invention relates to the hard-anodic-oxidation-coatings covering tool and hard-anodic-oxidation-coatings covering member which demonstrate the abrasion resistance which was excellent by covering a hard anodic oxidation coatings useful as surface-coating material of a heat proof and anti-corrosion members, such as the surface-coating material of the antifriction member as which high degrees of hardness, such as the surface-coating material of the cutting tool used for a manipulation of milling, a cutting, a piercing, etc. or metal mold, a bearing, a die, and a roll, are required or a screw for making machines, and a cylinder, and this hard anodic oxidation coatings.

[0002]

[Description of the Prior Art] When the cutting tool with which high abrasion resistance, such as a high speed steel and a cemented carbide tool, is demanded forms hard anodic oxidation coatings, such as TiN and TiC, in the base-material front face of a tool, wear-resistant enhancement is achieved. If the abrasion resistance of the above TiN and TiC is compared, TiN will be excellent in respect of [TiC] the oxidation resistance in a pyrosphere, and will demonstrate abrasion resistance to the crater of the tool rake face produced with the temperature increase by plastic working and frictional heat at the time of cutting. And TiN is excellent also in the adhesion with a base material. On the other hand, the degree of hardness of TiC is higher than TiN, and it has high endurance to the flank wear of the flank which touches ***ed material. However, even if oxidization start temperature was about 600 degrees C even if it was TiN excellent in oxidation resistance, and it was TiC which has a high degree of hardness, the Vickers hardness number is about 2000, and much more wear-resistant improvement was desired.

[0003] then -- for example, to JP,2-194159,A, aluminum which replaced a part of Ti by aluminum for the purpose of TiN, the oxidation resistance of TiC, or the enhancement in a degree of hardness, and the compound nitride and compound charcoal nitride [it is indicated as the following (aluminum, Ti) (C, N)] of Ti indicate -- having -- **** -- oxidization start temperature -- about 800 degrees C and Vickers hardness number -- about 2500 -- kg/mm2 ** -- the hard anodic oxidation coatings which shows the property to say is developed. However, in fields, such as a cutting as which much more high promotion of efficiency is required, the development of the hard anodic oxidation coatings which has the more excellent abrasion resistance was expected.

[0004]

[Problem(s) to be Solved by the Invention] It aims at offering the hard anodic oxidation coatings which demonstrates the abrasion resistance which this invention was made paying attention to such a situation, was excellent in oxidation resistance, without spoiling the base material adhesion which TiN coat has (C (aluminum, Ti), N), moreover has a high degree of hardness and was excellent.

[0005]

[Means for Solving the Problem] The hard anodic oxidation coatings excellent in the abrasion resistance concerning this invention which could attain the above-mentioned purpose is a coat formed in a base-material front face (Nz (Alx Ti1-x-y Siy) C1-z).

However, let it be a summary to consist of a chemical composition shown by $0.05 \leq x \leq 0.75$, $0.01 \leq y \leq 0.1$, $0.6 \leq z \leq 1$.

[0006] In addition, as for the thickness of the above-mentioned hard anodic oxidation coatings, it is desirable to make it 0.1-20 micrometers, and if the above-mentioned hard anodic oxidation coatings is formed in a base-material front face by the arc discharge method ion-plating method, it can obtain a hard-anodic-oxidation-coatings covering tool and a hard-anodic-oxidation-coatings covering member excellent in abrasion resistance.

[0007]

[Function] It aims at raising this invention persons' (C (aluminum, Ti), N) abrasion resistance much more. To the result (C (aluminum, Ti), N) which searched the alloying element effective in wear-resistant enhancement, the charcoal and the nitride which carried out minute amount inclusion of the Si have a high degree of hardness. And when satisfying $0.05 \leq x \leq 0.75$, $0.01 \leq y \leq 0.1$, and $0.6 \leq z \leq 1$ in the chemical formula which finds out that oxidization start temperature also becomes high and is shown with composition (NzC(Alx Ti1-x-y Siy)1-z) of a hard anodic oxidation coatings It traced demonstrating the abrasion resistance which became the oxidation-resistant good hard anodic oxidation coatings, and was excellent in the high degree of hardness, and this invention was completed.

[0008] Since the hard anodic oxidation coatings which furthermore starts this invention does not spoil the outstanding base-material adhesion which TiN has, either, when it applies to base-material front faces, such as metal mold, and a tool, an antifriction member, the problem of sublation does not arise, but it can obtain the hard-anodic-oxidation-coatings covering tool and hard-anodic-oxidation-coatings covering member which demonstrate the abrasion resistance of a coat enough.

[0009] In addition, it is thought that it is because the oxidization of Ti which starts by making Si contain as the 3rd metallic element at the time of an elevated temperature is suppressed or the protective film which consists of an aluminum oxide is remarkably made precise although the hard anodic oxidation coatings of this invention was not necessarily fully solved as ground for demonstrating the abrasion resistance which was excellent compared with the conventional coat.

[0010] Composition of the metallic element which constitutes the hard anodic oxidation coatings of this invention requires that x and y should satisfy conditional expression $0.05 \leq x \leq 0.75$ and $0.01 \leq y \leq 0.1$ in (Alx Ti1-x-y Siy), respectively. The value of x is less than 0.05, or oxidation-resistant enhancement effect with the value of y sufficient by less than 0.01 cannot be acquired. Moreover, if the value of x exceeds 0.75 or the value of y exceeds 0.1, the crystal

structure of a coat will change from a cubic to hexagonal, coat hardness falls, and sufficient abrasion resistance is not obtained. In addition, as a lower limit of x , 0.25 is desirable, and it is more desirable that it is 0.56 or more. As an upper limit of x , 0.75 is desirable, and it is more desirable that it is 0.7 or less. As a lower limit of y , 0.01 is desirable, and it is more desirable that it is 0.02 or more. As an upper limit of y , 0.08 is desirable, and it is more desirable that it is 0.05 or less.

[0011] Moreover, although the abrasion resistance which was excellent even if this invention was the nitride of the above-mentioned metallic element and it was charcoal and a nitride is demonstrated, in the case of charcoal and the nitride, it is required for the rate of an atomic ratio of nitrogen to be 60% or more. Namely, $N_z C_{1-z}$ It is required to satisfy $0.6 < z < 1$, and when the value of z is less than 0.6, the oxidation resistance of a coat will fall. In addition, oxidation resistance will become better if the value of z is 0.8 or more.

[0012] As thickness of the hard anodic oxidation coatings in the case of covering to a base material, it is desirable that it is [0.1 micrometers or more] 20 micrometers or less. If it is less than 0.1 micrometers, abrasion resistance cannot demonstrate enough, but when 20 micrometers is exceeded on the other hand, a crack may go into a hard anodic oxidation coatings with impulse force, and it is not desirable. In addition, when applying to a cutting tool, in order to obtain the abrasion resistance which employed the property of the cutting edge of tool base-material original efficiently, and was excellent, 8 micrometers or less are preferably expected still preferably 1 micrometers or more of 12 micrometers or less of the thickness of a hard anodic oxidation coatings still preferably about 2 micrometers or more and an upper limit. Moreover, although this invention does not limit the quality of the material of the base material which forms a hard anodic oxidation coatings, in order to exhibit the abrasion resistance which covered with sufficient adhesion on the base-material front face, and was excellent in it, hard matter, such as a cemented carbide, a high speed tool steel, a die steel, a cermet, and a ceramic, is suitable.

[0013] In addition, what is necessary is just to use the technique of illustrating below, in adopting the arc discharge formula ion-plating method, for example, although the PVD represented by the ion-plating method, the sputtering method, etc. is mentioned as the technique of forming the hard anodic oxidation coatings concerning this invention in a base-material front face. That is, it is the metal component of aluminum, Ti, and Si which were made to ionize by arc discharge from the cathode which is an evaporation source N_2 The ambient atmosphere and/or CH_4 It can obtain by carrying out an ion plating in the ambient atmosphere, and if the target of the coat composition made into the purpose and the same metal composition is used, the coat of the stable composition will be easy to be obtained. Moreover, if bias potential is impressed to a substrate, since the adhesion of a coat can be raised much more, it is desirable. In addition, although especially this invention does not limit gas ** at the time of an ion plating, either, about 1×10^{-3} to 5×10^{-2} Torr are desirable, and if it is this within the limits, the wear-resistant precise hard anodic oxidation coatings of high crystallinity which was excellent much more will be easy to be obtained.

[0014] Although an example is explained below, this invention not being limited to the following example, marking a front and the after-mentioned meaning, and changing suitably is included in the technical domain of this invention.

[0015]

[Example]

In order to investigate the oxidation resistance of example 1 coat, equip an arc discharge method ion plating system with the base material which consists of the dimension 7mmx25mm platinum foil, and it heats at 400 degrees C. While a metallic element is evaporated from the cathode of the various composition shown in Table 1 It is N_2 as reactant gas. Gas, or N_2 / CH_4 The test piece which covered with the thickness of 5 micrometers the coat of the various composition shown in Table 1 was produced by introducing mixed gas, and considering as the ambient atmosphere of 7×10^{-3} Torr, and impressing the potential of -150V to a base material.

[0016] While composition of a coat was searched for by electronic ***** X-ray microanalysis and the Auger electron spectroscopy, the oxidation test was performed on the following conditions. A result is shown in Table 1. (Conditions of an oxidation test)

Temperature-requirement: Room temperature - 1300 degree-C programming-rate:10 degrees C / min ambient atmosphere : A dry air, atmospheric pressure air-flow-rate:150cc/min [0017]

[Table 1]

No.	カソード材質	反応ガス	皮膜組成	酸化開始温度 (°C)	硬さ (Hv)	備考
1	$Al_{0.6}Ti_{0.4}$	N_2	$(Al_{0.6}Ti_{0.4})N$	820	272	従来例
2	$Al_{1.65}Ti_{0.35}Si_{0.005}$	N_2	$(Al_{0.7}Ti_{0.29}Si_{0.007})N$	820	2490	
3	$Al_{0.59}Ti_{0.4}Si_{0.01}$	N_2	$(Al_{0.6}Ti_{0.39}Si_{0.01})N$	913	3040	
4	$Al_{0.59}Ti_{0.4}Si_{0.01}$	N_2/CH_4	$(Al_{0.6}Ti_{0.39}Si_{0.01})(N_{0.4}C_{0.2})$	873	3190	実施例
5	$Al_{0.57}Ti_{0.33}Si_{0.05}$	N_2	$(Al_{0.57}Ti_{0.33}Si_{0.05})N$	1023	2950	
6	$Al_{0.57}Ti_{0.33}Si_{0.05}$	N_2/CH_4	$(Al_{0.57}Ti_{0.33}Si_{0.05})(N_{0.9}C_{0.1})$	950	3050	
7	$Al_{0.34}Ti_{0.35}Si_{0.1}$	N_2	$(Al_{0.34}Ti_{0.35}Si_{0.1})N$	1103	2750	比較例
8	$Al_{0.48}Ti_{0.32}Si_{0.2}$	N_2	$(Al_{0.5}Ti_{0.3}Si_{0.2})N$	1120	1900	

[0018] To oxidation starting N (aluminum, Ti) coat (No.1) of the conventional example at 820 degrees C, each oxidation start temperature of the hard anodic oxidation coatings (No.3-7) concerning this invention is 870 degrees C or more, and its oxidation resistance is improving so that clearly from Table 1. No.2 are an example of a comparison when there are few amounts of Si, and the oxidation-resistant enhancement with low oxidation start temperature does not accept.

[0019] The test piece was produced by the same technique as an example 1 except setting thickness of a coat to 10 micrometers, using a superhard chip as example 2 base material. When the micro Vickers hardness of the coat formed in the test piece was measured by 100g of loads, the result written together to Table 1 was obtained. The coat (No.3-7) concerning this invention shows the higher degree of hardness as compared with N coat (No.1) which is the

conventional example (aluminum, Ti) so that more clearly than Table 1. On the other hand, No.8 are an example of a comparison when there are too many amounts of Si, and since the crystal structure of a coat is changing from the cubic to hexagonal, coat hardness is falling remarkably.

[0020] The two sheet blade end mill with an outer diameter of 10mm was produced, having used example 3 cemented carbide as the base material, and the hard anodic oxidation coatings of the composition shown in Table 2 was formed in the cutting-part front face of each end mill by the thickness of 4 micrometers. Only No.2 formed the other hard anodic oxidation coatings by the arc discharge method ion-plating method, using the ion-plating method of a crucible vacuum evaporation method as the formation technique of a hard anodic oxidation coatings. As membrane formation conditions of an arc discharge method, substrate temperature was made into 400 degrees C, each impressed bias voltage -150V, and reactant gas formed membranes by 7×10^{-3} Torr.

[0021] Using the obtained hard-anodic-oxidation-coatings covering end mill, the cutting examination of the following conditions was performed and the abrasion loss of an end-mill cutting-edge flank was measured. A result is shown in Table 2 and the drawing 1.

(Cutting conditions)

Cutting Technique: **ed [side face cutting down cutting] material : SKD11 (hardness HB219)

Infeed : Rd 1mmxAd It sends 10mm cutting-speed:60m / , and min. : 0.07mm / tooth (270mm/min)

Cutting oil : air blow length of cut : 20m [0022]

[Table 2]

№	成膜方法	皮膜組成	送り面摩耗量 (mm)	備考
1	アーク放電方式IP法	(Al _{0.5} Ti _{0.4})N	0.055	従来例 実施例
2	ふっば蒸着方式IP法	Ti (N _{0.8} C _{0.2})	0.140	
3	アーク放電方式IP法	(Al _{0.5} Ti _{0.29} Si _{0.01})N	0.338	
4	アーク放電方式IP法	(Al _{0.58} Ti _{0.39} Si _{0.03})N	0.332	
5	アーク放電方式IP法	(Al _{0.57} Ti _{0.38} Si _{0.05})N	0.329	
6	アーク放電方式IP法	(Al _{0.54} Ti _{0.36} Si _{0.1})N	0.347	
7	アーク放電方式IP法	(Al _{0.5} Ti _{0.3} Si _{0.2})N	0.210	比較例

[0023] As compared with the conventional example (No. 1, 2), there are few amounts of flank wears and the hard-anodic-oxidation-coatings covering end mill (No.3-6) concerning this invention is excellent in the abrasion resistance to a flank wear so that clearly from the result of Table 2 and the drawing 1. They are an example of a comparison when there are too many amounts of Si, No.7 have many amounts of flank wears, and its abrasion resistance is not enough.

[0024] The JIS drill with an outer diameter of 10mm was produced, having used the high speed tool steel equivalent to example 4 JIS SKH51 as the base material, and the hard anodic oxidation coatings which shows composition in Table 3 on a drill cutting-part front face by the same technique as an example 3 was formed.

[0025] Using the obtained hard-anodic-oxidation-coatings covering drill, the cutting examination of the following conditions was performed and the cutting life was investigated. A result is shown in Table 3.

(Cutting conditions)

Cutting Technique: A hole down manipulation, **ed [5 each cutting] material : S55C (hardness HB220)

Cutting-speed: Send 30m / min. : 0.15mm/rev cutting length:30mm (through hole)

Cutting oil : water-soluble emulsion type cutting oil [0026]

[Table 3]

№	成膜方法	皮膜組成	平均穴割け 回数	備考
1	アーク放電方式IP法	(Al _{0.5} Ti _{0.4})N	638	従来例 実施例
2	ふっば蒸着方式IP法	Ti (N _{0.8} C _{0.2})	322	
3	アーク放電方式IP法	(Al _{0.5} Ti _{0.29} Si _{0.01})N	755	
4	アーク放電方式IP法	(Al _{0.58} Ti _{0.39} Si _{0.03})N	888	
5	アーク放電方式IP法	(Al _{0.57} Ti _{0.38} Si _{0.05})N	866	
6	アーク放電方式IP法	(Al _{0.54} Ti _{0.36} Si _{0.1})N	792	
7	アーク放電方式IP法	(Al _{0.5} Ti _{0.3} Si _{0.2})N	180	比較例

[0027] As compared with the conventional example (No. 1, 2), there is much mean hole down number and the hard-anodic-oxidation-coatings covering drill (No.3-6) concerning this invention has a long cutting life so that clearly from the result of Table 3. They are an example of a comparison when there are too many amounts of Si, No.7 have little mean hole down number, and its a cutting life is short.

[0028] metal mold equivalent to example 5 JIS SKD61 -- using material, the base material (No.1-3) with a dimension of 40x20x5mm was produced, and the hard anodic oxidation coatings with a thickness of 5 micrometers was formed in each base material by the same technique as an example 1 TiN coat was formed in the base material of No.1, N coat was formed in the base material of No.2 (aluminum0.5Ti0.5), N coat was formed in the base material of No.3 (aluminum0.58Ti0.39Si0.03), the thermal cycling test was performed on condition that the following, and endurance was

investigated as shown in Table 4. A result is shown in Table 4.

(Thermal-cycling-test conditions)

Thermostat: 800 degree C - Holding-time: 110 second cryostat: Water cooling - Holding time: 10 seconds [0029]

[Table 4]

符号	組成	クラック発生サイクル数	備考
1	TiN	150	従来例
2	(Al _{0.3} Ti _{0.3})N	635	
3	(Al _{0.55} Ti _{0.35} Si _{0.05})N	960	実施例

[0030] The hard anodic oxidation coatings (No.3) concerning this invention shows the property which was excellent also to the heat cycle as compared with the hard anodic oxidation coatings (No. 1, 2) of the conventional example a passage clear from the result of Table 4.

[0031]

[Effect of the Invention] this invention is constituted as mentioned above, the hard anodic oxidation coatings which shows the abrasion resistance and the oxidation resistance which were excellent even if it compared with conventional TiN coat and conventional N (Ti, aluminum) coat will be obtained, and the high degree-of-hardness member which demonstrates the abrasion resistance and the oxidation resistance which were excellent by covering the above-mentioned hard anodic oxidation coatings on a member front face further can be offered.

[Translation done.]

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(54)【発明の名称】 耐摩耗性に優れた硬質皮膜、硬質皮膜被覆工具及び硬質皮膜被覆部材

(57)【要約】

【目的】 TiN皮膜の有する母材密着性を損なうことなく、(Al, Ti) (C, N) より耐酸化性に優れしかも高硬度を有して優れた耐摩耗性を発揮する硬質皮膜を提供する。

【構成】 基材表面に形成される皮膜であって、

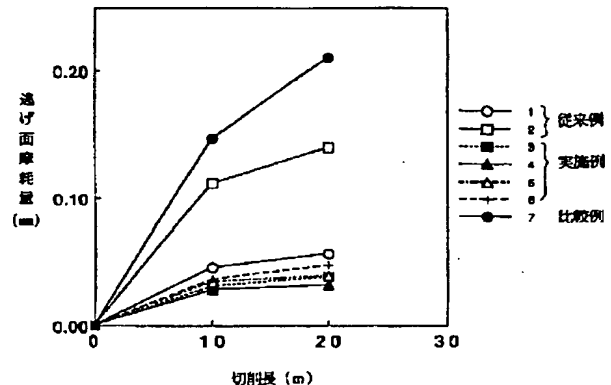
$(Al_x Ti_{1-x-y} Si_y) (N_z C_{1-z})$

但し、 $0.05 \leq x \leq 0.75$

$0.01 \leq y \leq 0.1$

$0.6 \leq z \leq 1$

で示される化学組成からなる。尚上記硬質皮膜の厚さは $0.1 \sim 20 \mu m$ にすることが好ましく、また上記硬質皮膜を、アーク放電方式イオンプレーティング法により基材表面に形成すれば耐摩耗性に優れた硬質皮膜被覆工具及び硬質皮膜被覆部材を得ることができる。



【特許請求の範囲】

【請求項1】 基材表面に形成される皮膜であって、
 $(Al_x Ti_{1-x-y} Si_y) (N_z Cl_{1-z})$

但し、 $0.05 \leq x \leq 0.75$

$0.01 \leq y \leq 0.1$

$0.6 \leq z \leq 1$

で示される化学組成からなることを特徴とする耐摩耗性に優れた硬質皮膜。

【請求項2】 皮膜の厚さが $0.1 \sim 20 \mu m$ である請求項1記載の硬質皮膜。

【請求項3】 請求項1または2記載の硬質皮膜を、アーク放電方式イオンプレーティング法により基材表面に形成してなることを特徴とする耐摩耗性に優れた硬質皮膜被覆工具及び硬質皮膜被覆部材。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、フライス加工、切削加工、穿孔加工等の加工に使用される切削工具の表面被覆材、或は金型、軸受け、ダイス、ロールなど高硬度が要求される耐摩耗部材の表面被覆材、もしくは成形機用スクリーやシリンダ等の耐熱・耐食部材の表面被覆材として有用な硬質皮膜、及び該硬質皮膜を被覆することによって優れた耐摩耗性を発揮する硬質皮膜被覆工具及び硬質皮膜被覆部材に関するものである。

【0002】

【従来の技術】高速度工具や超硬合金工具など高い耐摩耗性が要求される切削工具は、工具の基材表面にTiNやTiC等の硬質皮膜を形成することにより耐摩耗性の向上が図られている。上記TiNとTiCの耐摩耗性を比較すると、TiNは高温域における耐酸化性の点でTiCより優れており、切削時の加工熱や摩擦熱によって生じる工具すくい面のクレータ摩耗に対して耐摩耗性を発揮する。しかもTiNは母材との密着性にも優れている。一方TiCはTiNより硬度が高く、被削材と接する逃げ面のフランク摩耗に対して高い耐久性を有している。しかしながら耐酸化性に優れたTiNであっても酸化開始温度は $600^\circ C$ 程度であり、また高い硬度を有するTiCであってもそのビッカース硬さは 2000 程度であり、耐摩耗性の一層の改善が望まれていた。

【0003】そこで例えば特開平2-194159には、TiNやTiCの耐酸化性や硬度の向上を目的として、Tiの一部をAlに置換したAl, Tiの複合窒化物や複合炭窒化物〔以下 $(Al, Ti) (C, N)$ と示す〕が開示されており、酸化開始温度は約 $800^\circ C$ 、ビッカース硬さは約 $2500 kg/mm^2$ という特性を示す硬質皮膜が開発されている。但し一層の高効率化が要求されている切削加工などの分野では、より優れた耐摩耗性を有する硬質皮膜の開発が期待されていた。

【0004】

【発明が解決しようとする課題】本発明はこうした事情

に着目してなされたものであって、TiN皮膜の有する母材密着性を損なうことなく、 $(Al, Ti) (C, N)$ より耐酸化性に優れしかも高硬度を有して優れた耐摩耗性を発揮する硬質皮膜を提供することを目的とするものである。

【0005】

【課題を解決するための手段】上記目的を達成し得た本発明に係る耐摩耗性に優れた硬質皮膜とは、基材表面に形成される皮膜であって、

$(Al_x Ti_{1-x-y} Si_y) (N_z Cl_{1-z})$

但し、 $0.05 \leq x \leq 0.75$

$0.01 \leq y \leq 0.1$

$0.6 \leq z \leq 1$

で示される化学組成からなることを要旨とするものである。

【0006】尚上記硬質皮膜の厚さは $0.1 \sim 20 \mu m$ にすることが好ましく、また上記硬質皮膜を、アーク放電方式イオンプレーティング法により基材表面に形成すれば耐摩耗性に優れた硬質皮膜被覆工具及び硬質皮膜被覆部材を得ることができる。

【0007】

【作用】本発明者らは $(Al, Ti) (C, N)$ の耐摩耗性をより一層向上させることを目的として、耐摩耗性向上に有効な添加元素を検索した結果、 $(Al, Ti) (C, N)$ にSiを微量含有させた炭・窒化物は硬度が高く、しかも酸化開始温度も高くなることを見出し、硬質皮膜の組成が $(Al_x Ti_{1-x-y} Si_y) (N_z Cl_{1-z})$ で示される化学式において $0.05 \leq x \leq 0.75$ 、 $0.01 \leq y \leq 0.1$ 、 $0.6 \leq z \leq 1$ を満足する場合は、高硬度で耐酸化性の良好な硬質皮膜となり優れた耐摩耗性を発揮することを突き止め、本発明を完成させた。

【0008】さらに本発明に係る硬質皮膜はTiNの有する優れた基材密着性も損なうことがないので、金型や工具および耐摩耗部材等の基材表面に適用した場合も剥離の問題が生じず、皮膜の耐摩耗性を十分発揮する硬質皮膜被覆工具及び硬質皮膜被覆部材を得ることができる。

【0009】尚本発明の硬質皮膜が従来の皮膜に比べて優れた耐摩耗性を発揮する理由としては十分に解明されたわけではないが、Siを第3の金属元素として含有させることにより高温時におけるTiの酸化を抑制したり、Al酸化物からなる保護皮膜を著しく緻密化するかからであると考えられる。

【0010】本発明の硬質皮膜を構成する金属元素の組成は、 $(Al_x Ti_{1-x-y} Si_y)$ においてx, yが夫々 $0.05 \leq x \leq 0.75$ 、 $0.01 \leq y \leq 0.1$ という条件式を満足することが必要である。xの値が0.05未満であるか、またはyの値が0.01未満では十分な耐酸化性の向上効果を得ることができない。またxの

値が0.75を超えるか、またはyの値が0.1を超えると皮膜の結晶構造が立方晶から六方晶へ変化してしまい、皮膜硬さが低下して十分な耐摩耗性が得られない。なお、xの下限値としては0.25が好ましく、0.56以上であることがより望ましい。xの上限値としては0.75が好ましく、0.7以下であることがより望ましい。yの下限値としては0.01が好ましく、0.02以上であることがより望ましい。yの上限値としては0.08が好ましく、0.05以下であることがより望ましい。

【0011】また本発明は上記金属元素の窒化物であっても炭・窒化物であっても優れた耐摩耗性を発揮するが、炭・窒化物の場合、窒素の原子比率が60%以上であることが必要である。即ち $N_z C_{1-z}$ で $0.6 \leq z \leq 1$ を満足することが必要であり、zの値が0.6未満の場合は皮膜の耐酸化性が低下してしまう。尚、zの値が0.8以上であると耐酸化性がより良好となる。

【0012】基材に被覆する場合の硬質皮膜の厚さとしては、 $0.1 \mu m$ 以上 $20 \mu m$ 以下であることが好ましい。 $0.1 \mu m$ 未満であると耐摩耗性が十分発揮できず、一方 $20 \mu m$ を超えると衝撃力によって硬質皮膜にクラックが入ることがあり、望ましくない。なお、切削工具に適用する場合、工具基材本来の切れ刃の特性を生かし且つ優れた耐摩耗性を得るには、硬質皮膜の厚さを好ましくは $1 \mu m$ 以上、更に好ましくは $2 \mu m$ 以上、また上限について $12 \mu m$ 以下、更に好ましくは、 $8 \mu m$ 以下が望まれる。また本発明は硬質皮膜を形成する基材の材質を限定するものではないが、基材表面に密着性よく被覆し、優れた耐摩耗性を発揮させるためには超硬合金や高速度工具鋼、ダイス鋼、サーメット、セラミック等の硬質物質が適している。

【0013】尚本発明に係る硬質皮膜を基材表面に形成する方法としては、イオンプレーティング法やスパッタリング法等に代表されるPVD法が挙げられるが、例えばアーク放電式イオンプレーティング法を採用する場合には以下に例示する方法を用いればよい。即ち、アーク放電により蒸発源であるカソードからイオン化させたA

1, TiおよびSiの金属成分を、 N_2 雰囲気および/または CH_4 雰囲気中でイオンプレーティングすることによって得ることができ、目的とする皮膜組成と同一金属組成のターゲットを使用すれば、安定した組成の皮膜が得られ易い。また基板にバイアス電位を印加すると、皮膜の密着性を一段と高めることができるので好ましい。尚、本発明はイオンプレーティング時のガス圧も特に限定するものではないが、 $1 \times 10^{-3} \sim 5 \times 10^{-2}$ Torr程度が好ましく、この範囲内であれば耐摩耗性の一段と優れた高結晶性の緻密な硬質皮膜が得られ易い。

【0014】以下実施例について説明するが、本発明は下記の実施例に限定されるものではなく、前・後記の趣旨に徴して適宜変更することは本発明の技術的範囲に含まれる。

【0015】

【実施例】

実施例1

皮膜の耐酸化性を調べるため、寸法 $7 mm \times 25 mm$ の白金箔からなる基材をアーク放電方式イオンプレーティング装置に装着して $400^\circ C$ に加熱し、表1に示す種々の組成のカソードから金属元素を蒸発させると共に、反応ガスとして N_2 ガスあるいは N_2 / CH_4 混合ガスを導入して 7×10^{-3} Torrの雰囲気とし、且つ基材に $-150 V$ の電位を印加することによって表1に示す種々の組成の皮膜を $5 \mu m$ の厚さで被覆した試験片を作製した。

【0016】電子プローブX線マイクロアナリシスおよびオージェ電子分光法により皮膜の組成を求めると共に、下記条件で酸化試験を行った。結果は表1に示す。

(酸化試験の条件)

温度範囲：室温 $\sim 1300^\circ C$

昇温速度： $10^\circ C/min$

雰囲気：乾燥空気、大気圧

空気流量： $150 cc/min$

【0017】

【表1】

No.	カソード材質	反応ガス	皮 膜 組 成	酸化開始温度 (℃)	硬 さ (Hv)	備 考
1	$Al_{0.6}Ti_{0.4}$	N_2	$(Al_{0.6}Ti_{0.4})N$	820	2720	従来例
2	$Al_{0.69}Ti_{0.30}Si_{0.005}$	N_2	$(Al_{0.7}Ti_{0.29}Si_{0.007})N$	820	2480	
3	$Al_{0.59}Ti_{0.4}Si_{0.01}$	N_2	$(Al_{0.6}Ti_{0.39}Si_{0.01})N$	910	3040	実 施 例
4	$Al_{0.59}Ti_{0.4}Si_{0.01}$	N_2/CH_4	$(Al_{0.6}Ti_{0.39}Si_{0.01})(N_{0.8}C_{0.2})$	870	3180	
5	$Al_{0.57}Ti_{0.38}Si_{0.05}$	N_2	$(Al_{0.57}Ti_{0.38}Si_{0.05})N$	1020	2950	
6	$Al_{0.57}Ti_{0.38}Si_{0.05}$	N_2/CH_4	$(Al_{0.57}Ti_{0.38}Si_{0.05})(N_{0.9}C_{0.1})$	950	3060	
7	$Al_{0.54}Ti_{0.36}Si_{0.1}$	N_2	$(Al_{0.54}Ti_{0.36}Si_{0.1})N$	1100	2750	
8	$Al_{0.48}Ti_{0.32}Si_{0.2}$	N_2	$(Al_{0.5}Ti_{0.3}Si_{0.2})N$	1120	1900	比較例

【0018】表1から明らかなように、従来例の(Al , Ti) N 皮膜(No. 1)は、820℃で酸化が開始するのに対し、本発明に係る硬質皮膜(No. 3~7)の酸化開始温度はいずれも870℃以上であり、耐酸化性が向上している。No. 2は Si 量が少ない場合の比較例であり、酸化開始温度が低く耐酸化性の向上が認められない。

【0019】実施例2

基材として超硬チップを用い、皮膜の厚みを10μmにする以外は、実施例1と同じ方法で試験片を作製した。試験片に形成された皮膜のマイクロビッカース硬さを荷重100gで測定したところ、表1に併記する結果が得られた。表1より明らかなように、本発明に係る皮膜(No. 3~7)は従来例である(Al , Ti) N 皮膜(No. 1)と比較してより高い硬度を示している。一方、No. 8は Si 量が多過ぎる場合の比較例であり、皮膜の結晶構造が立方晶から六方晶へ変化している為、皮膜硬さが著しく低下している。

【0020】実施例3

超硬合金を基材として外径10mmの2枚刃エンドミルを作製し、夫々のエンドミルの刃部表面に表2に示す組成の硬質皮膜を4μmの厚さで形成した。硬質皮膜の形

成方法としては、No. 2だけはるつば蒸着方式のイオンブレイティング法を用い、それ以外の硬質皮膜はアーク放電方式イオンブレイティング法により形成した。アーク放電方式の成膜条件としてはいずれも、基板温度を400℃とし、バイアス電圧を-150V印加し、反応ガスは 7×10^{-3} Torrで成膜した。

【0021】得られた硬質皮膜被覆エンドミルを用いて、下記条件の切削試験を行ない、エンドミル切れ刃逃げ面の摩耗量を測定した。結果は表2および図1に示す。

(切削条件)

切削方法：側面切削ダウンカット

被削材：SKD11(硬さHB219)

切込み：Rd 1mm×Ad 10mm

切削速度：60m/min

送り：0.07mm/tooth(270mm/min)

切削油：エアーブロー

切削長：20m

【0022】

【表2】

No	成膜方法	皮膜組成	逃げ面摩耗量 (mm)	備 考
1	アーク放電方式IP法	(Al _{0.6} Ti _{0.4})N	0.056	従来例
2	るつば蒸着方式IP法	Ti(N _{0.8} C _{0.2})	0.140	
3	アーク放電方式IP法	(Al _{0.6} Ti _{0.39} Si _{0.01})N	0.038	実 施 例
4	アーク放電方式IP法	(Al _{0.58} Ti _{0.39} Si _{0.03})N	0.032	
5	アーク放電方式IP法	(Al _{0.57} Ti _{0.38} Si _{0.05})N	0.039	
6	アーク放電方式IP法	(Al _{0.54} Ti _{0.36} Si _{0.1})N	0.047	
7	アーク放電方式IP法	(Al _{0.5} Ti _{0.3} Si _{0.2})N	0.210	比較例

【0023】表2および図1の結果から明らかなように、本発明に係る硬質皮膜被覆エンドミル(No. 3~6)は、従来例(No. 1, 2)と比較して逃げ面摩耗量が少なくフランク摩耗に対する耐摩耗性が優れている。No. 7はSi量が多過ぎる場合の比較例であり、逃げ面摩耗量が多く、耐摩耗性が十分でない。

【0024】実施例4

JIS規格SKH51相当の高速工具鋼を基材として外径10mmのJIS規格ドリルを作製し、実施例3と同じ方法でドリル刃部表面に表3に組成を示す硬質皮膜を形成した。

【0025】得られた硬質皮膜被覆ドリルを用いて、下

記条件の切削試験を行ない切削寿命を調べた。結果は表3に示す。

(切削条件)

切削方法：穴明け加工、各5本切削

被削材：S55C(硬さHB220)

切削速度：30m/min

送り：0.15mm/rev

切削長さ：30mm(貫通穴)

切削油：水溶性エマルジョン型切削油

【0026】

【表3】

No	成膜方法	皮膜組成	平均穴明け 個数	備 考
1	アーク放電方式IP法	(Al _{0.6} Ti _{0.4})N	638	従来例
2	るつば蒸着方式IP法	Ti(N _{0.8} C _{0.2})	322	
3	アーク放電方式IP法	(Al _{0.6} Ti _{0.39} Si _{0.01})N	755	実 施 例
4	アーク放電方式IP法	(Al _{0.58} Ti _{0.39} Si _{0.03})N	988	
5	アーク放電方式IP法	(Al _{0.57} Ti _{0.38} Si _{0.05})N	866	
6	アーク放電方式IP法	(Al _{0.54} Ti _{0.36} Si _{0.1})N	792	
7	アーク放電方式IP法	(Al _{0.5} Ti _{0.3} Si _{0.2})N	180	比較例

【0027】表3の結果から明らかなように、本発明に係る硬質皮膜被覆ドリル(No. 3~6)は、従来例(No. 1, 2)と比較して平均穴明け個数が多く切削寿命が長い。No. 7はSi量が多過ぎる場合の比較例であり、平均穴明け個数が少なく、切削寿命が短い。

【0028】実施例5

JIS規格SKD61相当の金型材を用いて、寸法40×20×5mmの基材(No. 1~3)を作製し、夫々の基材に実施例1と同様の方法で厚さ5μmの硬質皮膜を形成した。表4に示すとおり、No. 1の基材にはT

iN皮膜を形成し、No. 2の基材には(Al_{0.5}Ti_{0.5})N皮膜を形成し、No. 3の基材には(Al_{0.58}Ti_{0.39}Si_{0.03})N皮膜を形成し、下記の条件で熱サイクル試験を行ない耐久性を調査した。結果は表4に示す。

(熱サイクル試験条件)

高温槽：800℃ 保持時間：110秒

低温槽：水冷 保持時間：10秒

【0029】

【表4】

符号	皮膜組成	クラック発生サイクル数	備考
1	TiN	150	従来例
2	(Al _{0.5} Ti _{0.5})N	635	
3	(Al _{0.58} Ti _{0.39} Si _{0.03})N	960	実施例

【0030】表4の結果から明らかな通り、本発明に係る硬質皮膜（No. 3）は従来例の硬質皮膜（No. 1, 2）と比較して熱サイクルに対しても優れた特性を示す。

【0031】

【発明の効果】本発明は以上の様に構成されており、従来のTiN皮膜や(Ti, Al)N皮膜と比較しても優

れた耐摩耗性および耐酸化性を示す硬質皮膜が得られることとなり、さらに上記硬質皮膜を部材表面に被覆することにより優れた耐摩耗性及び耐酸化性を発揮する高硬度部材が提供できることとなった。

【図面の簡単な説明】

【図1】実施例で得た表面被覆工具の逃げ面摩耗量と切削長の関係を表すグラフである。

【図1】

